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(54) COPOLYMER AND ADHESIVE FILM PREPARED THEREFROM

(71) We, TH. GOLDSCHMIDT A.G. a German Body Corporate of 43 Essen, Goldschmidtstrasse 100, Germany,

do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

The invention relates to a copolymer and an adhesive film comprising the copolymer, which film is non-tacky at room temperature and can be activated, and is self-crosslinking at elevated temperatures, and which can optionally be bonded to a plastic film.

Film-like or sheet-like adhesives are advantageously used for gluing sheet-like constructional materials. Such sheet-like adhesives permit precise control of the amount of adhesive over the entire area to be glued. It also avoids the use of solvents. To carry out the gluing operation, the supported adhesive films or unsupported adhesive sheets are introduced between the workpieces to be glued together, after which the workpieces are pressed against one another at an elevated temperature.

This gluing technique initially found acceptance in the timber industry, for example in the plywood industry. For gluing the individual layers of wood, so-called glue films are used. Glue films in general consist of a paper carrier web which is impregnated and coated with phenoplast or aminoplast resin precondensates.

Adhesive films have also proved of value in gluing metals. Particularly for gluing metals to one another, adhesive films have been disclosed in which a carrier web is impregnated with the solution of a phenol-formaldehyde precondensate resin and is covered with thermoplastic on both sides. This thermoplastic essentially has the function of plasticising the resin which has cured in the glue-line, and to counteract its embrittlement. Such an adhesive film, and a process for the manufacture of such an adhesive film, are described in German Patentschrift 1,212,240. According to this, a porous carrier is impregnated with a solution of a curable condensation resin, and the tacky and still moist carrier is coated, so as to cover the surface practically completely, on one or both sides with pulverulent or granular thermoplastics or a corresponding film and is then dried at temperatures below the curing conditions of the condensation resin. Preferably, a glass fibre fleece is used as the carrier web.

For many cases, however, it is desirable to use unsupported adhesive films. This may be

due to the mechanical strength of the adhesive film but optical reasons may also be of decisive importance. An unsupported film additionally has the advantage that the glue-like can be kept thinner than is possible when using a supported adhesive film.

The present invention is concerned with a particular copolymer and an adhesive film comprising this copolymer, which film is non-tacky at room temperature but can be activated, and is self-crosslinking, at an elevated temperature, especially at temperatures above 100°C. This desired film should, as far as possible, be capable of indefinite storage at room temperature without curing.

In particular, the invention is concerned with developing an unsupported adhesive film which can be used as an adhesive for metals. If a plastic film is to be glued to a metal surface it is desirable that the adhesive film can be formed on the plastic film or vice versa, so that in use it is not necessary to handle two separate films, but only one laminate film.

The present invention provides a copolymer of

a) 1 to 60% by weight of acrylonitrile and/or methacrylonitrile,

b) 30 to 95% by weight of an acrylic acid alkyl ester with 1 to 12 carbon atoms in the alkyl radical,

c) 1 to 15% by weight of acrylic acid, methacrylic acid and/or itaconic acid and

d) 0.1 to 20% by weight of a N-alkoxyalkylamide of acrylic acid and/or methacrylic acid, the sum of the constituents a), b), c) and d) amounting to 100% by weight.

The present invention also provides an adhesive film which is non-tacky at room temperature and can be activated, and is self-crosslinking, at an elevated temperature, comprising a copolymer of the invention.

The crosslinking principle on which the copolymer according to the invention is based is described in German Patentschrift 1,011,850 and 1,035,363 and in the literature, for example in the journal "Die makromolekulare Chemie" 57, (1961), pages 27 to 51.

Acrylic acid alkyl esters, of which the alkyl radical has 2 to 4 carbon atoms, are particularly preferred for use. Accordingly, preferred acrylic acid alkyl esters are acrylic acid ethyl ester, acrylic acid propyl ester and acrylic acid butyl ester, the n-butyl ester being particularly preferred.

Preferably, a compound with lower alkoxy radicals and/or alkyl radicals is used as the N-alkoxyalkylamide of acrylic acid and/or methacrylic acid. The alkoxy radical can in general contain 1 to 4 carbon atoms. The methyl radical is of particular importance as an alkyl radical. Higher alkyl radicals are used rarely. The N-methoxymethylamide of acrylic acid or methacrylic acid is particularly preferred. Good results are also obtained when using the N-butoxymethylamide of acrylic acid and/or methacrylic acid.

The copolymer is suitably prepared in a manner which is in itself known by polymerisation of the monomers in solution, suspension or dispersion. Equally, the film formation as such, from the copolymer obtained, is to be carried out in a manner which is in itself known. It can be effected by casting the solution of the polymer and evaporating the solvent. In the case of suspension polymerisation, the suspended particles are freed from water and the film is suitably produced by extrusion or calendering.

The film according to the invention, having the above-mentioned composition, is colourless and transparent. This is of very considerable technical importance especially in cases where a polymer film which is also transparent is to be glued, for example onto a metal substrate, by means of this adhesive film. The absence of colour of this film is also particularly desirable if the film is to be dyed with soluble dyestuffs or pigments, since the original colour shade of the dyestuff or pigment is only preserved if the adhesive film is colourless. Particularly when manufacturing adhesive films provided with white pigments it is important that the film should be colourless, since even slight discolorations considerably detract from the degree of whiteness of the film. Additionally to the pigments, or in place of the pigments, it is possible to add fillers, such as calcium carbonate, calcium sulphate, pyrogenically produced silica, barium sulphate, magnesium oxide, aluminium oxide, asbestos powder or fibres or other fillers which are in themselves known, to the film, in which case the film of course loses its transparency.

As a result of the combination of the N-alkoxyalkylamide of acrylic acid and/or methacrylic acid with acrylic acid or methacrylic acid and/or itaconic acid, the adhesive film cures, the curing taking place the more rapidly, the higher is the temperature. The curing of the film is suitably carried out at temperatures above 80°C, preferably in a temperature range from about 140 to 170°C. If the film is used for gluing together metal sheets and coating films (so-called coil coating), temperatures of up to 250°C may be employed briefly.

The curing of the copolymer of the invention can be assisted by the addition of extraneous crosslinking substances, of which the amount added should in general not exceed 25% by weight based on the weight of constituents a), b), c) and d). Such extraneous crosslinking substances are, in particular, epoxy resins or aminoplast or phenoplast resin precondensates. As epoxy resins, expoxides of poly-unsaturated hydrocarbons, glycidyl ethers of

polyhydric alcohols, epoxide ethers of polyhydric phenols, glycidyl esters of unsaturated carboxylic acids or their anhydrides and epoxidised oils having an alcohol radical of 1 to 18 carbon atoms have quite generally proved suitable.

Aminoplast resin precondensates which can be used are the reaction products of urea and/or thiourea and/or melamine with formaldehyde. The reaction products which have been etherified with lower alcohols are also suitable. The precondensates are present in the so-called B-state, that is to say they can still be fused before they cure irreversibly. A similar behaviour is shown by the phenoplast resin precondensates, for which the condensation products of phenol or phenol derivatives with formaldehyde are used. The film obtained is then no longer colourless. The tensile shear strength of the glue-line is improved by adding the epoxy resins and/or the aminoplast or phenoplast resin precondensates.

The adhesive film of the invention can additionally contain up to 25% by weight of a polyamide, based on the weight of constituents a), b), c) and d). This improves the peel strength of the glue-line. A copolyamide of equal parts of caprolactam, hexamethylenediamine/adipic acid and p,p′-diaminodicyclohexylmethane/adipic acid, or a copolyamide of 60% by weight of adipic acid/hexamethylenediamine and 40% by weight of caprolactam, has proved particularly suitable.

The film according to the invention fulfils the initially presented requirements. It permits the production of glue bonds of high shear strength, coupled with high peel strength, and the low temperature resistance and heat resistance of the glue-line should be singled out particularly. This is explained in yet further detail in the Examples below.

It is particularly advantageous that the adhesive film can, before gluing to the metal surface, be bonded to a film which forms a protective layer, or that the adhesive film can be produced on this film, so that such a laminate film can be used directly on metal, for example sheet metal, in order to carry out the coil coating process. The particular advantage of using such a laminate film for the coil coating process is that the surface-protection layer is already in a finished form and that both it and the adhesive layer are solvent-free. This avoids disturbing the adhesive bond. At the same time, the expensive equipment for eliminating the solvents, which is always necessary, in accordance with the state of the art, when liquid adhesives and/or liquid coating resins are used, becomes superflous.

A particularly advantageous film finished in accordance with the sense of the present invention is therefore one which is bonded on one side to a thermoplastic film. As the thermoplastic film it is possible to use films of polyvinyl halide or polyvinylidene halide, preferably of polyvinyl chloride or polyvinyl fluoride. Films based on polyacrylic acid esters and/or polymethacrylic acid esters and acrylonitrile/butadiene/styrene copolymers are also suitable.

Such a laminate film can be manufactured by first producing, according to one of the known techniques, a film of the thermoplastic material and then applying to this film the solution or dispersion of the copolymer to be used according to the invention, so producing the adhesive film according to the invention on the thermoplastic film. It is also possible to follow the converse procedure by applying the solution or dispersion of the thermoplastic polymer to the adhesive film according to the invention and forming the second layer by evaporating the solvent or the water from the dispersion.

Instead of being bonded to a thermoplastic film, the adhesive film can also be bonded on one side to a curable or cured film.

The film according to the invention is particularly suitable for gluing the heat-curable unsupported surface-protective films according to German Patentschrift 1,961,452 or Offenlegungsschrift 2,212,928.

The film according to the teaching of German Patentschrift 1,961,452 consists of a mixture of an elastomeric copolymer A and a hard and brittle copolymer B and is one in which the copolymer A has been manufactured by copolymerisation of

a) 70 to 99% by weight of an acrylic acid alkyl ester of which the alkyl radical has 1 to 8 carbon atoms,

b) 1 to 20% by weight of an unsaturated monocarboxylic acid or of an anhydride of an unsaturated dicarboxylic acid, optionally

c) 0 to 20% by weight of a vinyl monomer which on homopolymerisation gives a hard and brittle polymer, especially styrene, acrylonitrile or methyl methacrylate and optionally

d) 0 to 2% by weight of a crosslinking monomer having at least two reactive, non-conjugated double bonds in the molecule,

and in which copolymer B is manufactured by copolymerisation of

a) 60 to 70% by weight of styrene or of a methacrylic acid alkyl ester of which the alkyl radical has 1 to 4 carbon atoms,

b) 1 to 20% by weight of a glycidyl ester of acrylic acid or methacrylic acid,

c) 1 to 20% by weight of an unsaturated monocarboxylic acid or of an anhydride of an unsaturated dicarboxylic acid, optionally

d) 0 to 20% by weight of a vinyl monomer which on homopolymerisation gives a hard and brittle polymer, especially styrene, acrylonitrile or methyl methacrylate, and optionally

e) 0 to 3% by weight of vinyl pyridine,

the weight ratio of the elastomeric copolymer A to the hard and brittle copolymer B being 1 : 20 to 1 : 3.

Experiments have shown that in conjunction with the adhesive film the copolymer B in itself already forms an outstandingly suitable curable surface layer and that the copolymer A does not necessarily have to be present when coating metal surfaces, if the adhesive film according to the invention is used.

The film according to German Offenlegungsschrift 2,212,928 consists of

I: an elastomeric copolymer having a glass transition temperature of at most +10°C or below, which has been obtained by copolymerisation of

a) 70 to 99% by weight of an acrylic acid alkyl ester with 1 to 8 carbon atoms in the alkyl radical,

b) 1 to 20% by weight of a hydroxyalkyl ester with 2 to 4 carbon atoms in the alkyl radical and/or of an acid amide of acrylic acid or methacrylic acid and optionally

c) 0 to 2% by weight of a crosslinking monomer with at least two reactive non-conjugated double bonds in the molecule, it being possible for the reactivity of the two double bonds to differ from one another, the sum of a), b) and c) being 100% by weight, as the grafting base, onto which has been granted

II: a hard and brittle copolymer, obtained by copolymerisation of

a) 60 to 80% by weight of styrene and/or a methacrylic acid alkyl ester with 1 to 20 carbon atoms in the alkyl radical,

b) 1 to 20% by weight of an acrylic acid alkyl ester with 1 to 8 carbon atoms in the alkyl radical,

c) 1 to 20% by weight of a N-methoxymethylamide of acrylic acid and/or methacrylic acid,

d) 1 to 20% by weight of a hydroxyalkyl ester of acrylic acid or methacrylic acid with 2 to 4 carbon atoms in the alkyl radical,

e) 1 to 20% by weight of acrylic acid amide or meth-acrylic acid amide, the molar ratio of the components c) to the sum of d) and e) being about 1 : 1 and the ratio of d) : e) being 4 : 1 to 1 :4, and optionally

f) 0 to 20% by weight of acrylonitrile, the sum of the components a) to f) being 100% by weight, and the weight ratio of the elastomeric copolymer I to the hard and brittle copolymer II being 1 : 3 to 1 : 20.

In this case again it suffices merely to use the hard and brittle copolymer II by itself for the production of the surface-protective films.

With regard to the manufacture of the films according to German Patentschrift 1,961,452 or according to German Offenlegungsschrift 2,212,928, reference may be made to the particular publications.

A further aspect of the invention provides a method of bonding two surfaces together which comprises applying a film according to the invention, to one of the surfaces, heating the film to a curing temperature e.g. to above 80°C, especially to 140° to 170°C, and bringing the film covered surface into contact with the second surface before or after the film is cured.

To use the adhesive film according to the invention, which is bonded on one side to a curable film, for coating metal surfaces, it is not absolutely essential that the curing of the film which forms the surface-protective layer should take place during or after the gluing process. It is also possible already to cure the surface-protective layer at an earlier point in time, for example during the manufacture of the laminate film. The film still has sufficient elasticity to permit its processing, and especially gluing-down and subsequent shaping of a metal sheet protected with such a laminate film, without damaging the surface-protective layer.

The manufacture of the polymer, the manufacture of the film and the processing and properties of the film according to the invention are explained in more detail in the Examples which follow.

Example 1

Manufacture and test of an adhesive film

a) Manufacture of the polymer in solution

One-fifth of a mixture of 70 parts by weight of acrylonitrile, 120 parts by weight of ethyl acrylate, 17.2 parts by weight of acrylic acid, 15.4 parts by weight of N-methoxymethylmethacrylamide, 170 parts by weight of ethylene chloride, 30 parts by weight of methanol and 0.3 part by weight of dodecylmercaptan is freed from dissolved oxygen by boiling under reflux in nitrogen. 0.4 part by weight of azodiisobutyronitrile is

then added and the mixture is heated to 80°C. After reaching a conversion of about 10%, the remaining 4/5 of the above-mentioned mixture are added dropwise over a period of 10 hours. After a total reaction time of 30 hours a conversion of 98.5% is reached.

The Staudinger index, determined in chloroform at 20°C, is 0.32 [100 ml/g]. The polymer is soluble in benzene, methylene chloride, acetone, ethyl acetate and tetrahydrofurane.

b) Preparation of the adhesive film

A 100 μ thick film is cast from the resulting solution by pouring out onto a polytetrafluoroethylene-coated metal sheet and then evaporating the solvent; this film is flexible, transparent, colourless and non-tacky at room temperature.

c) Technological test

Test specimens are produced according to DIN 53,281 with the films obtained and with metal sheets according to DIN 1,783-Al Cu Mg 2 pl F 41, and these are examined in the angle-peel test according to DIN 53,282, in respect of bond strength under tension according to DIN 53,283 and in respect of drum-peel strength and drum-peel torque according to DIN 53,289. The angle-peel strength, tensile shear strength, drum-peel strength and drum-peel torque as a function of the temperature are shown in the table below:

Temperature °C	Angle-peel strength [kp/mm]	Tensile shear strength [k/mm²]	Drum-peel strength [kp/mm]	Drum-peel torque [kp·mm/mm]
25	0.70	3.0		
50	0.34	1.2		
80		0.66		
20			25.2	29.85
0			20.2	23.30
−20			17.4	19.25

Example 2

Manufacture and test of an adhesive film

The copolymer is manufactured as in Example 1a). Before casting it to form a film as described in Example 1b), the substances indicated in the table below are added to the copolymer solution, and the angle-peel strength and tensile shear strength at 25°C are determined as indicated under 1 c).

Additive	% by weight	Angle-peel strength [kp/mm¹]	Tensile shear strength [kp/mm²]
Calcium carbonate	25	0.735	2.13
	10	0.20	3.10
Polyamide	20	0.35	3.75
	30	0.41	3.85
Epoxide resin	10	0.49	2.95
	20	0.72	3.20

Example 3

Manufacture and test of an adhesive film

a) Manufacture of the polymer in suspension

To a mixture of 75 parts by weight of acrylonitrile, 120 parts by weight of n-butyl acrylate, 8.6 parts by weight of itaconic acid, 7.6 parts by weight of methoxymethyl-methacrylamide, 0.3 part by weight of dodecylmercaptan and 0.4 part by weight of azodiisobutyronitrile were added to 39.8 parts by weight of a polymer which had been obtained using the monomer mixture just indicated, in solution, in accordance with Example 1 a); a viscous solution is thus obtained. This is dispersed by stirring in a solution of 4 parts by weight of polyvinyl alcohol and 450 parts by weight of distilled water and the suspension is warmed to 60°C under a stream of nitrogen. The polymerisation is complete after 5 hours and the bead polymer obtained is filtered off, repeatedly washed with distilled water and finally with methanol, and then dried *in vacuo*.

The Staudinger index, determined in chloroform at 20°C, is 0.36 [100 ml/g]. The polymer is soluble in benzene, methylene chloride, acetone, ethyl acetate and tetrahydrofurane.

b) Manufacture of the film

The bead polymer is kneaded at 90°C and then calendered between polytetrafluoroethylene-coated rollers. A 100 μ thick, flexible, transparent, colourless film which is non-tacky at room temperature is obtained.

c) Technological test

The dependence of the drum-peel strength on the temperature is determined as in Example 1 c):

Temperature °C	Drum-peel strength [kp/mm]	Drum-peel torque [kp·mm/mm]
20	28.95	26.37
0	22.13	19.93
−20	17.35	15.90

Example 4

Manufacture of a laminate film

a) Manufacture of the copolymer of the surface-protective layer, in the form of a film

A mixture of 224 parts by weight of methylene chloride and 96 parts by weight of methanol is freed from dissolved oxygen by boiling under reflux in nitrogen. 233.2 parts by weight of methyl methacrylate, 34.5 parts by weight of n-butyl methacrylate, 20.9 parts by weight of methyl acrylate, 20.9 parts by weight of methoxymethyl methacrylamide, 6.8 parts by weight of methylacrylamide, 10.5 parts by weight of hydroxyethyl methacrylate and 32.9 parts by weight of stearyl methacrylate are then added to the solvent mixture; the batch is again freed from dissolved oxygen by boiling under reflux. 0.72 part by weight of azodiisobutyronitrile is then added and the mixture is stirred for 12 hours at 60°C, whereby a conversion of 98% is achieved.

The Staudinger index of the resulting copolymer, determined in chloroform at 20°C, is 1.85 [100 ml/g]. The polymer is soluble in benzene, methylene chloride, acetone, ethyl acetate and tetrahydrofurane.

A 50 μ thick film is cast from this solution after adding 36 parts by weight of butylglycol butyl phthalate, 0.9 part by weight of methoxyphenylbenztriazole, 1.8 parts by weight of a butyl-etherified melamine resin, 0.72 part by weight of p-toluenesulphonic acid and 1.4 parts by weight of release agent. The tensile impact strength (DIN 53,448) and the pendulum hardness according to König (DIN 53,157) of this film at room temperature is 40 [kp. cm/cm^2] and 135 [secs.] respectively, in the uncured state and 43 [kp. cm/cm^2] and 145 [secs.] respectively in the cured state (heating to 145°C for 10 minutes). The swelling index (H. Dannenberg and W. H. Harp jr., Anal. Chem. 28 (1956) 86), determined after standing for 24 hours in an atmosphere of 1,2-dichloroethane, is 1.65 after heating to 150°C for 10 minutes.

b) Manufacture of the laminate film and coating of galvanised steel

The copolymer solution from Example 1 a) is cast onto the film from 4 a) so that after

evaporating the solvent at 50°C a 40 μ thick layer is produced. The resulting laminate film is pressed for 3 minutes at 165°C under a pressure of 20 [kp/cm^2] onto a carefully degreased and bonderised galvanised steel sheet.

c) Technological test

The sheet coated in this way was subjected to the following tests:

Condensate water/varying climatic conditions with an atmosphere containing SO_2 (Kesternich test according to DIN 50,018). Assessment after 46 cycles: gloss has decreased from initially 85% to 50%, but in other respects the surface is completely intact and free from rust; no significant migration under a cross-cut.

Salt spray mist test (DIN 50,021): no findings after 1,000 hrs.

Condensate water test (DIN 50,017): no findings after 1,000 hrs.

Erichsen deep-drawing test (DIN 53,156): > 10 mm.

Bending test: T = 1.5; perfect condition, no formation of hairline cracks, very slight white fracture.

Dish test: perfect condition, very slight white fracture.

After exposing the coated dish at 90°C for 1 hour, the film does not detach from the edge.

Example 5

Manufacture of a laminate film

a) Manufacture of the copolymer of the surface-protective layer in the form of a pigmented film

The procedure followed is as in Example 4 a) but additionally a concentrate of titanium oxide (rutile) in the copolymer solution is prepared as follows: 25.4 parts by weight of methylene chloride and 10.8 parts by weight of methanol are freed from dissolved oxygen by boiling under reflux in nitrogen. 71.5 parts by weight of titanium oxide, 18.9 parts by weight of methyl methacrylate, 2.7 parts by weight of n-butyl methacrylate, 1.6 parts by weight of methyl acrylate, 1.6 parts by weight of methoxymethylmethacrylamide, 0.5 part by weight of hydroxyethyl methacrylate, 0.5 part by weight of methacrylamide, 2.6 parts by weight of stearyl methacrylate and 0.4 part by weight of dodecylmercaptan are then added to the solvent mixture and oxygen is then removed in the usual manner. Thereafter, 0.4 part by weight of azodiisobutyronitrile are added and the solution is stirred for 10 hours at 60°C, whereby a 99% conversion is achieved.

The copolymer solution obtained according to 4 a) is mixed with this pigment concentrate by simple stirring; 1.84 parts by weight of release agent, 3.68 parts by weight of butyl-etherified melamine-formaldehyde resin, 1.15 parts by weight of methoxyphenylbenztriazole and 0.92 part by weight of p-toluenesulphonic acid are added thereto.

A film 100 μ thick is cast from this solution; its tensile impact strength and pendulum hardness at room temperature, in the uncured state, are 38 [kp. cm/cm^2] and 138 [secs.], respectively. The swelling index is 1.55.

b) Manufacture of the laminate film and coating of an aluminium sheet

The copolymer solution from Example 1 a) is cast onto the film moistened with methylene chloride (solvent content about 20%) so that a 25 μ thick layer is produced after removing the solvent. The laminate film obtained is pressed for 45 seconds at 220°C under a pressure of 30 [kp/cm^2] onto a carefully degreased and bonderised aluminium sheet.

Example 6

Manufacture of a laminate film

a) Manufacture of the copolymer used to form the pigmented laminate film

In contrast to Example 1 a), the adhesive copolymer is manufactured in the presence of cadmium selenide red, by reacting one-fifth of a mixture of 70 parts by weight of acrylonitrile, 120 parts by weight of ethyl acrylate, 25.8 parts by weight of acrylic acid, 15.4 parts by weight of methoxymethyl-methacrylamide, 170 parts by weight of ethylene chloride, 30 parts by weight of methanol and 0.3 part by weight of dodecylmercaptan, in the presence of 50 parts by weight of cadmium selenide which has been dispersed in the mixture by means of a stirrer which produces high shear forces, at 80°C after addition of 0.1 part by weight of azodiisobutyronitrile. After reaching a conversion of 10%, the remaining 4/5 of the monomer mixture are added dropwise over a period of 10 hours. After a total reaction time of 23 hours, a conversion of 99% is reached.

b) Manufacture of the laminate film and coating onto steel

The pigmented copolymer solution obtained according to Example 6 a) is cast on a polytetrafluoroethylene-coated base. After evaporating off a part of the solvent, the solution of the copolymer obtained according to Example 4 a) is cast onto this film in such a way

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that after complete removal of the solvent a layer thickness of 40 μ results. The thickness of the adhesive layer is 35 μ. The laminate film obtained is pressed for 35 seconds at 230°C, under a pressure of 30 [kp/cm²], onto carefully degreased and bonderised steel sheet.

Example 7

Manufacture of a laminate film

a) Manufacture of the graft copolymer of the surface-protective layer, in film form

A) A mixture of 56 parts by weight of methylene chloride and 24 parts by weight of methanol is freed from dissolved oxygen by boiling under reflux. Thereafter, 36.2 parts by weight of n-butyl acrylate, 3.7 parts by weight of hydroxyethyl methacrylate, 0.08 part by weight of allyl methacrylate and 0.04 part by weight of ethyleneglycol dimethacrylate are added to the solvent mixture; nitrogen is again passed through for 1 hour and the polymerisation is then initiated with 0.08 part by weight of azodiisobutyronitrile. The mixture is stirred under nitrogen at 60°C for 6 hours, whereby a conversion of 85% is achieved.

B) In a second stage, 210.2 parts by weight of methyl methacrylate, 23.0 parts by weight of styrene, 10.5 parts by weight of acrylonitrile, 34.5 parts by weight of n-butyl methacrylate, 20.9 parts by weight of methyl acrylate, 20.9 parts by weight of methoxymethylmethacrylamide, 6.8 parts by weight of methacrylamide, 10.5 parts by weight of hydroxyethyl methacrylate and 32.9 parts by weight of stearyl methacrylate are dissolved in 229 parts by weight of methylene chloride and 96 parts by weight of methanol in the presence of the elastomeric copolymer A) produced above. The mixture is next again freed from dissolved oxygen by boiling under reflux. 0.72 part by weight of azodiisobutyronitrile is then added and the mixture is stirred for 12 hours at 60°C, whereby a conversion of 98% is achieved.

The Staudinger index, determined in chloroform at 20°C, is 1.28 [100 ml/g]. The polymer is soluble in benzene, methylene chloride, acetone, ethyl acetate and tetrahydrofurane.

A 100 μ thick film is cast from this solution after adding 39 parts by weight of dibutyl phthalate, 1.5 parts by weight of methoxyphenylbenztriazole, 2.1 parts by weight of a butyl-etherified melamine resin, 0.8 part by weight of p-toluenesulphonic acid and 1.6 parts by weight of a release agent based on fluorine. The tensile impact strength and the pendulum hardness of this film at room temperature, in the uncured state, are 98 [kp. cm/cm²] and 130 [secs.] respectively, whilst in the cured state they are 60 [kp. cm/cm²] and 135 [secs.] respectively. The swelling index, after heating to 150°C for 10 minutes, is 2.0.

b) Manufacture of the copolymer for the adhesive film

The procedure followed is as in Example 6 a).

c) Manufacture of the laminate film and coating of galvanised steel

The copolymer solution from Example 6 a) is cast onto the film from 7 a) so that after evaporating the solvent at 50°C a 40 μ thick layer is produced. The resulting laminate film is pressed for 3 minutes at 165°C under a pressure of 20 [kp/cm²] onto a carefully degreased and bonderised galvanised steel sheet.

Example 8

Manufacture of a laminate film

a) Manufacture of the graft copolymer of the surface protective layer, in film form

The procedure followed is as in Example 7. The reaction mixture has the following composition:

A) 36.22 parts by weight of n-butyl acrylate
3.70 parts by weight of hydroxyethyl methacrylate
0.08 part by weight of allyl methacrylate
56.00 parts by weight of methylene chloride
24.00 parts by weight of methanol
0.08 part by weight of azodiisobutyronitrile

Conversion: 85% after 5 hours at 60°C

B) 288.60 parts by weight of n-butyl methacrylate
20.90 parts by weight of methoxymethyl-methacrylamide
6.80 parts by weight of methacrylamide
10.50 parts by weight of hydroxyethyl methacrylamide
32.90 parts by weight of stearyl methacrylate
224.00 parts by weight of methylene chloride
96.00 parts by weight of methanol
0.72 part by weight of azodiisobutyronitrile

Conversion: 99% after 11 hours at 60°C

The Staudinger Index, determined in chloroform at 20°C, is 2.05 [100 ml/g]. The polymer is soluble in benzene, methylene chloride, acetone, ethyl acetate and tetrahydrofurane.

A 50μ thick film is cast from this solution after adding 36 parts by weight of ethylphthalyl glycollate, 1.5 parts by weight of methoxyphenylbenztriazole, 2.1 parts by weight of a butyl-etherified melamine resin, 0.8 part by weight of p-toluenesulphonic acid and 1.6 parts by weight of a release agent based on fluorine. The tensile impact strength and the pendulum hardness of this film at room temperature, in the uncured state, are 150 [kp. cm/cm^2] and 25 [secs.] respectively, whilst in the cured state they are 130 [kp. cm/cm^2] and 30 [secs.] respectively. The swelling index, after heating to 150°C for 10 minutes, is 2.3.

b) Manufacture of the copolymer of the adhesive film

The procedure followed is as in Example 6 a) except that instead of cadmium selenide, green chromium oxide was employed.

c) Manufacture of the laminate film and coating of galvanised steel

The copolymer solution from Examples 8 b) is cast onto the film from 8 a) so that after evaporating the solvent at 50°C a 40 μ thick layer is produced. The resulting laminate film is pressed for 3 minutes at 165°C under a pressure of 20 [kp/cm^2] onto a carefully degreased and bonderised galvanised steel sheet.

Example 9

Manufacture of a laminate film

a) Manufacture of the copolymer of the surface-protective layer in film form

300 parts by weight of xylene and 300 parts by weight of methyl ethyl ketone are freed from dissolved oxygen by boiling under reflux. 67 parts by weight of methyl methacrylate, 12.5 parts by weight of styrene, 12.8 parts by weight of n-butyl acrylate, 2.4 parts by weight of acrylonitrile, 15.2 parts by weight of glycidyl methacrylate, 7.2 parts by weight of acrylic acid and 1.5 parts by weight of dicumyl peroxide are added thereto. The batch is stirred at 85°C under nitrogen; after a reaction time of 12 hours, a further 0.75 part by weight of dicumyl peroxide is added. After a total of 26 hours, a conversion of 98% is found after precipitation with a five-fold amount of methanol.

The Staudinger index, determined in chloroform at 20°C is 1.70 (100 ml/g]. The polymer is soluble in benzene, methylene chloride, acetone, ethyl acetate and tetrahydrofurane.

A 100 μ thick film is cast from this solution after adding 9 parts by weight of butylglycol butyl phthalate, 0.4 part by weight of methoxyphenylbenztriazole, 0.6 part by weight of a butyl-etherified melamine resin and 0.4 part by weight of a release agent based on fluorine. The tensile impact strength and pendulum hardness of this film at room temperature in the uncured state is 42 [kp. cm/cm^2] and 135 [secs.] respectively. The swelling index, after heating to 150°C for 10 minutes, is 2.10.

b) Manufacture of the pigmented copolymer of the adhesive film
The procedure followed is as in Example 8 b).

c) Manufacture of the laminate film and coating of galvanised steel
The copolymer solution from Example 8 b) is cast onto the film from 9 a) so that after evaporating the solvent at 50°C a 40 μ thick layer is produced. The resulting laminate film is pressed for 3 minutes at 165°C under a pressure of 20 ≤kp/cm^2] onto a carefully degreased and bonderised galvanised steel sheet.

Example 10

Manufacture of a laminate film
A commercially available polyvinylfluoride film, 50 μ thick, is coated by the casting process with a 15 μ thick layer of the copolymer manufactured according to Example 1 a). The laminate film obtained is pressed for 2 minutes at 165°C, under a pressure of 20 [kp/cm^2], onto a carefully degreased and bonderised aluminium sheet.

The following Table summarises the results of Technological tests of the coated metal sheets from Examples 5 to 10.

	Film from Example No.:					
	5	6	7	8	9	10
Kesternich test after 45 cycles (DIN 50,018)	Intact surface, no significant migration under a cross-cut	Intact, rustfree surface, no significant migration under a cross-cut	Intact, rustfree surface, no significant migration under a cross-cut	Intact, rustfree surface, no significant migration under a cross-cut	Intact rustfree surface, no significant migration under a cross-cut	Intact surface, no significant migration under a cross-cut
Decrease in gloss, Gardner method	85 →50%	85 →55%	85 →35%	85 →35%	85 →50%	--
Salt spray test after 1,000 hrs (DIN 50,021)	No findings	No findings	No findings	No findings	No findings	No findings
Condensate water test after 1,000 hrs (DIN 50,017)	No findings	No findings	No findings	No findings	No findings	No findings
Brief weathering in Xenotest 1,200 cycles 17/3 after 1,000 hrs	No chalking	No chalking	No chalking	No chalking	No chalking	--
Decrease in gloss, Gardner method	85 →80%	85 →80%	85 →75%	85 →75%	85 →80%	--

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	Film from Example No.:					
	5	6	7	8	9	10
Erichsen deep-drawing test (DIN 53, 156)	> 10 mm	> 10 mm	> 10 mm	> 10 mm	> 10 mm	> 10 mm
Bending test	T = 0; no hairline cracks, no white fracture	T = 1; no hairline cracks, no white fracture	T = 1.5; no hairline cracks, slight white fracture	T = 1.5; no hairline cracks, slight white fracture	T = 1.5; no hairline cracks, slight white fracture	——
Dish deep-drawing test	Perfect adhesion	Perfect adhesion	Perfect adhesion	Perfect adhesion	Perfect adhesion	Perfect adhesion
Exposure of a dish for 1 hour at 90°C	No detachment at the edge	No detachment at the edge	No detachment at the edge	No detachment at the edge	No detachment at the edge	No detachment at the edge

WHAT WE CLAIM IS:–

1. A copolymer of
a) 1 to 60% by weight of acrylonitrile and/or methacrylonitrile,
b) 30 to 95% by weight of an acrylic acid alkyl ester with 1 to 12 carbon atoms in the alkyl radical,
c) 1 to 15% by weight of acrylic acid, methacrylic acid and/or itaconic acid and
d) 0.1 to 20% by weight of a N-alkoxyalkylamide of acrylic acid and/or methacrylic acid, the sum of the constituents a), b), c) and d) amounting to 100% by weight.

2. A mixture comprising a copolymer as claimed in claim 1, and up to 25% by weight of an extraneous crosslinking substance based on the weight of constituents a), b), c) and d).

3. A mixture according to claim 2, wherein the extraneous crosslinking substance is an epoxy resin or an aminoplast or phenoplast resin precondensate.

4. A mixture comprising a copolymer as claimed in claim 1 or a mixture as claimed in claim 2 or 3 and up to 25% by weight of a polyamide based on the weight of constituents a), b), c) and d).

5. A mixture comprising a copolymer as claimed in claim 1 or a mixture as claimed in claim 2, 3 or 4 and a filler and/or a pigment.

6. A copolymer according to claim 1 substantially as described in any one of the Examples.

7. A cross-linked copolymer obtained by heating a copolymer as claimed in claim 1 or 6 or a mixture as claimed in any one of claims 2 to 5.

8. An adhesive film which is non-tacky at room temperature and can be activated, and is self-crosslinking, at an elevated temperature, comprising a copolymer as claimed in claim 1 or 6, a mixture as claimed in any one of claims 2 to 5 or a cross-linked copolymer as claimed in claim 7.

9. A film according to claim 8 which is unsupported.

10. A film according to claim 8 bonded to a plastic film.

11. A film according to claim 8 or 10 bonded on one side to a thermoplastic film.

12. A film according to claim 11, wherein the thermoplastic film is a polyvinyl halide film or an acrylonitrile/butadiene/styrene polymer film.

13. A film according to any one of claims 8 and 10 to 12 bonded on one side to a curable or cured film.

14. A film according to claim 8, substantially as hereinbefore described in any one of the Examples.

15. A method of preparing an adhesive film which is non-tacky at room temperature and can be activated and is self-crosslinking at an elevated temperature, which method comprises forming a copolymer by copolymerisation of
a) 1 to 60% by weight of acrylonitrile and/or methacrylonitrile,
b) 30 to 95% by weight of an acrylic acid alkyl ester with 1 to 12 carbon atoms in the alkyl radical,
c) 1 to 15% by weight of acrylic acid, methacrylic acid and/or itaconic acid and
d) 0.1 to 20% by weight of a N-alkoxyalkylamide of acrylic acid and/or methacrylic acid the sum of the constituents a), b), c) and d) amounting to 100% by weight and converting the resulting copolymer into a film.

16. A method according to claim 15, wherein the film additionally contains up to 25% by weight of an extraneous crosslinking substance based on the weight of constituents a), b), c) and d).

17. A method according to claim 16, wherein the extraneous crosslinking substance is an epoxy resin or an aminoplast or phenoplast resin precondensate.

18. A method according to any one of claims 15 to 17, wherein the film additionally contains up to 25% by weight of a polyamide based on the weight of constituents a), b), c) and d).

19. A method according to any one of claims 15 to 18, wherein a filler and/or a pigment is included in the film.

20. A method according to any one of claims 15 to 19, wherein the film is bonded to a plastic film.

21. A method according to any one of claims 15 to 20, wherein the film is bonded to one side of a thermoplastic film.

22. A method according to claim 21, wherein the thermoplastic film is a polyvinyl halide film or an acrylonitrile/butadiene/styrene polymer film.

23. A method according to any one of claims 15 to 20, wherein the film is bonded on one side to a curable or cured film.

24. A method according to any one of claims 15 to 23, wherein the film is heated to crosslink the copolymer.

25. A method according to claim 15, substantially as hereinbefore described with refer-

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nce to any one of th Examples.

26. A film obtained by a method according to any one of claims 15 to 25.

27. A method of bonding two surfaces together which comprises applying a film according to any one of claims 8 to 14 and 26 to one of the surfaces, heating the film to a curing temperature and bringing the film covered surface into contact with the second surface before or after the film is cured.

28. A method according to claim 27, wherein the film is cured after the two surfaces are placed in position for bonding.

29. A method according to claim 27, wherein the surfaces are metal and the two surfaces are placed in position for bonding after the film is cured.

30. A method according to any one of claims 27 to 29, wherein the film is heated to above 80°C.

31. A method according to claim 30, wherein the film is heated to 140 – 170°C.

32. A method according to claim 27, substantially as hereinbefore described in any one of the Examples.

33. Bonded articles obtained by a method according to any one of claims 27 to 32.

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